Thermal Stability of Metallic Single-Walled Carbon Nanotubes: An O(N) Tight-Binding Molecular Dynamics Simulation Study

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Abstract.
Order(N) Tight-Binding Molecular Dynamics (TBMD) simulations are performed to investigate the thermal stability of $(10, 10)$ metallic Single-Walled Carbon Nanotubes (SWCNT). Periodic boundary conditions (PBC) are applied in axial direction. Velocity Verlet algorithm along with the canonical ensemble molecular dynamics (NVT) is used to simulate the tubes at the targeted temperatures. The effects of slow and rapid temperature increases on the physical characteristics, structural stability and the energetics of the tube are investigated and compared. Simulations are carried out starting from room temperature and the temperature is raised in steps of 300K. Stability of the simulated metallic SWCNT is examined at each step before it is heated to higher temperatures. First indication of structural deformation is observed at 600K. For higher heat treatments the deformations are more pronounced and the bond breaking temperature is reached around 2500K. Gradual (slow) heating and thermal equilibrium (fast heating) methods give the value of radial thermal expansion coefficient in the temperature range between 300K-600K as $0.31 \times 10^{-5}(1/K)$ and $0.089 \times 10^{-5}(1/K)$, respectively. After 600K, both methods give the same value of $0.089 \times 10^{-5}(1/K)$. The ratio of the total energy per atom with respect to temperature is found to be $3 \times 10^{-4}eV/K$.

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1. Introduction

There has been increasing attention on nanotechnological research due to the demand for the most durable nanoscale structures in recent years. SWCNTs are in the first group of materials in this respect due to their high tensile strength and adjustable electrical conductivity. SWCNTs high thermal and chemical stability can conveniently be applied to gas sensors, dielectric devices, nanoelectronic devices, nanocomposites and emitters. SWCNTs high thermal stability can be compared with other single walled nanotubes. For example, Single Walled Aluminum Nitride Nanotubes (SWAlNNTs) can stabily exist at room temperature but start to melt when temperature is higher than 600 K [1]. This tendency to deform easily in the radial direction is a disadvantage for possible applications. On the other hand, studies on the high temperature stability of gold nanotubes show that they are barely stable up to 1200K with total energy per atom 2.8×10^{-4}eV/K [2,3]. Therefore there is an increasing attention on the thermal behavior of metallic CNTs which varies depending on their diameters, lengths and chiralities.

The available experimental and theoretical studies on thermal stability of SWCNTs show that they are still in an initial stage. The available results are limited and not in agreement with each other. A $4\mathring{A}$ diameter nanotube having a single vacancy with three dangling bonds has been found to retain its cylindrical shape at high temperatures around 4000 K [4]. Liew et al. [5] investigated the thermal properties of various CNTs using MD simulation method. They found that SWCNTs are thermally more stable than MWCNTs. They also showed that shorter CNTs are able to withstand higher thermal loads. CNTs with a larger diameter are also more resistant to thermal loads. On the other hand temperature affects the structural properties and energetics of CNTs. The coalescence of SWCNTs is investigated by Terrones et al. [6] using not only in situ under electron irradiation at high temperatures in TEM, but also by TBMD and Monte Carlo simulations. They observed that SWCNTs heated above $2000C^0$ in Ar or He atmospheres lead to either MWCNTs or coalesced SWCNTs of larger diameters. Metenier et al. [7] investigated the effect of thermal treatment under argon gas flow on the evolution of SWCNT bundles. Their experiments showed that the SWCNT bundles are not affected up to $1600C^0$, however, coalescence of SWCNTs starts to occur between $1800 - 2000C^0$. From the heat treatment at $2200C^0$, the disappearance of SWCNTs to the benefit of MWCNTs is observed. Same results are also observed in the experimental study by Yudasaka et al. [8]. In accord with these results an MD simulation is performed by Lopez et al. [9]. They showed that bundles of SWCNTs are stable under thermal treatment up to $1600C^0$. Above $2200C^0$ they become unstable and transform into MWCNTs. The effect of heat treatment on thermal stability and structural changes of DWCNTs is investigated by Kim et al. [10]. They showed that DWCNTs are structurally stable up to $2000C^0$. Between $2100 - 2400C^0$ the outer walls of adjacent DWNTs start coalescing into large diameter tubes. Between $2500 - 2800C^0$ MWNTs and flaky carbons were observed using experimental methods. Kawai et al. [11] also investigated the coalescence of Ultrathin Carbon Nanotubes (UTCNTs) using

TBMD simulation technique. They have found that above $2000C^0$, two UTCNTs having either the same chirality or different chiralities can coalesce without initially introducing atomic defects to enhance the reaction.

In this paper, we study the thermal history of a (10,10) SWCNT using our O(N), TBMD approach which previously proved to be successful in simulations of electronic structure and elastic properties of the same nanotube [12,13]. The effects of slow and rapid temperature increases on the physical characteristics, structural stability and the energetics of the tube are investigated and compared.

2. Method

The traditional TB solves the Schrödinger equation in reciprocal space by direct matrix diagonalization which results in cubic scaling with respect to the number of atoms. The O(N) methods on the other hand solve for the band energy in real space and make the approximation that only the local environment contributes to the bonding, and hence band energy, of each atom. In fact all the O(N) methods in which the properties of the whole system are computed such as the total energy or the forces on all atoms necessarily involve approximations to the exact solution of the effective one-electron Hamiltonian. These approximations are based on physical assumptions that are generally connected to the locality or near-sightedness principle in one way or another. The O(N) scaling arises from the decay and/or truncation of certain quantities. We have used TBMD algorithms involving an energy functional and a parametrization that was previously proven successful in heat applications [6]. In a previous work two of the authors (G. D. and C. Ö.) have improved and successfully applied the Order(N) techniques to these TBMD algorithms in simulations of SWCNTs. Details of the technique and the parametrization can be followed in [12-14] and the references therein.

In the present work a (10,10) single walled CNT consisting of 400 atoms with 20 layers is simulated using $O(N)$ parallel tight binding molecular dynamics algorithms. In the implementation of the $O(N)$ technique we adopted a Divide and Conquer approach. The accuracy of the description is enhanced by the use of basis functions of only the neighboring atoms that is called the "buffer". The Schrödinger equation of the buffer has the same form as in [14]. The eigenvalues and eigenvectors are found by diagonalizing the Hamilton matrix for each subsystem. Buffer size and the cuboidal box size (also called DAC box size) are the two important parameters of the $O(N)$ algorithms. We took the DAC box size equal to the distance between two consecutive cross-sectional layers ($1.229\mathring{A}$) along the uniaxial direction in a $(10, 10)$ tube [12]. This provides the same number of interacting neighbor atoms for each subsystem. Periodic boundary condition is applied in the uniaxial direction. All the simulations presented here are carried out in the canonical (N,V,T) ensemble. The Newtonian equations of motion are integrated using the Velocity Verlet algorithm with a time step equal to 1 fs. To avoid an inaccurate integration, the velocities of the constituent atoms are occasionally rescaled

to maintain the temperature of the system at the target value. The difference of $O(N^3)$ total energy result with $O(N)$ total energy result is indicated as error. By tuning the above two parameters we try to minimize the error. The errors for different buffer sizes are found for the $(10, 10)$ tube and the smallest error is read at the buffer size of $4.8\overset{\circ}{A}$ [15]. The time step of the simulations determines the real time of the simulation. Before starting the production phase of the simulations careful study of the time step is done. A time step that brings the system quickly to thermal equilibrium is chosen as 1 fs. It is also made sure that the possibility of the system getting trapped in a metastable state is avoided. Cut-offs for the interactions and the bond length, bond angle distribution functions are $2.6\overset{\circ}{A}$ and $2.1\overset{\circ}{A}$, respectively. It is known that temperature can be related to the average energy of a system of particles in equilibrium. This definition also works for nanoscale systems such as CNTs. MD simulations calculate the position and the velocity of each atom at each time step. We store the velocity values and compute the average kinetic energy over N steps in time:

$$< K.E. >= \frac{m}{2N} \sum_{n=1}^{N} v_i{}^2(t_n) =< \frac{1}{2}mv_i{}^2 > \quad . \tag{1}$$

Here the averaging must be done over very long times in order to obtain good statistical average kinetic energies. Then kinetic energy can be converted into a temperature scale using

$$< \frac{1}{2}mv_i{}^2 >= \frac{3}{2}k_B T_i \quad . \tag{2}$$

Thus the simulation temperature is controlled by rescaling the velocities.

3. Results and Discussion

During our simulations the SWCNTs were heated by two different methods. In the first method which is based on "gradual (slow) heating", the system has been brought to equilibrium at 300K temperature during a 5 ps of run. Thermal history applied to the SWCNT can be followed in Figure 1. Temperature has been increased in steps of 300K. System has been brought to equilibrium in 2 ps periods at each targeted temperature. Information about the strain energy of the tube at each temperature can be followed from this figure. As the temperature increased longer periods of relaxations are applied in order to observe the detachment of atoms from the $(10, 10)$ SWCNT. Bond breaking temperature is observed at 2500K. At this temperature, after 13 ps of relaxation one atom is detached and as the simulation proceeds, the number of detached atoms increased and a tearing effect is observed [15]. In Figure 1, sharp peaks after 13 ps of relaxations indicate the detachment of atoms. Starting from 600K, hexagons are deformed but carbon atoms kept their bonding until 2500K. In Figure 2 we present the change of total energy per atom with temperature. Kinetic energy, band-structure energy and the repulsive potential energy contributions to the total energy are also displayed in Figure 2. Kinetic energy and band-structure energy increase with temperature as expected. Repulsive potential energy decreases with
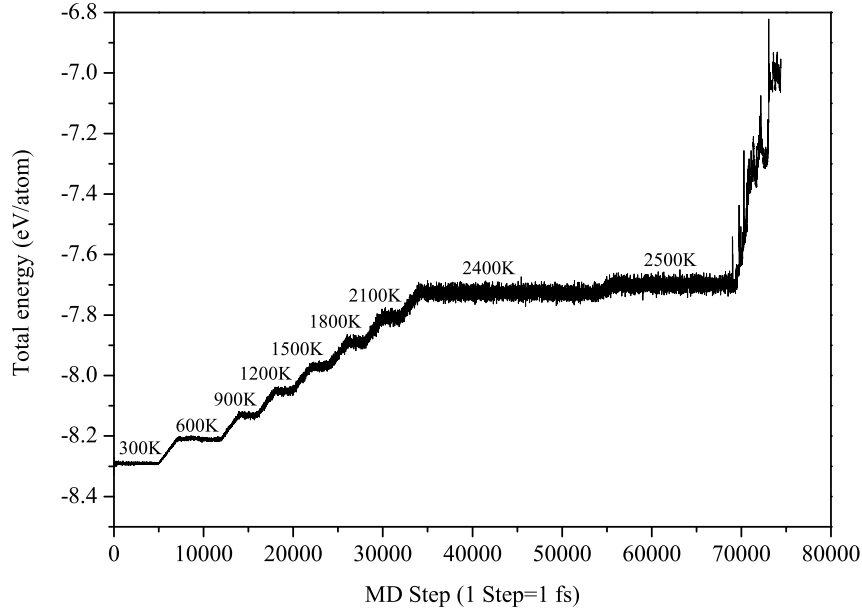
Figure 1. Thermal history of total energy per atom of (10,10) SWCNT as a function of simulation time in gradual heating. Tube decays at 2500K.
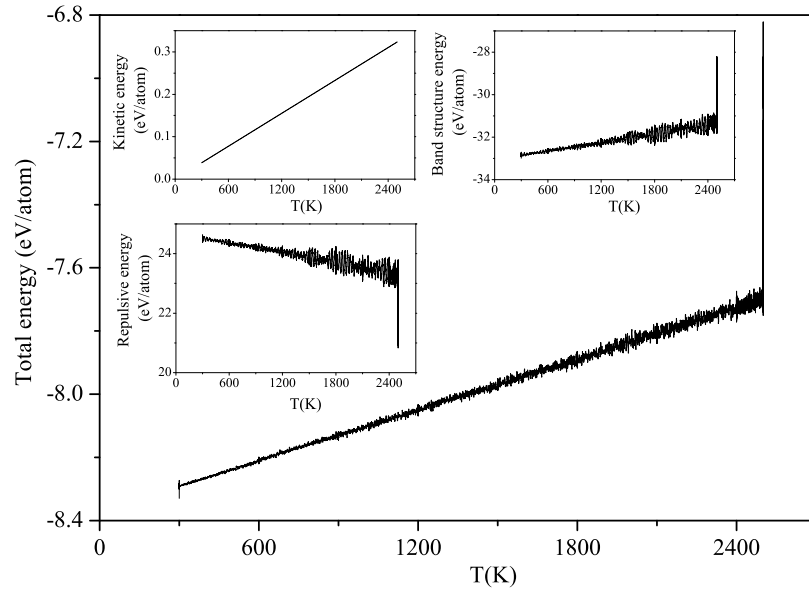

Figure 2. Total energy per atom as a function of temperature. Kinetic energy, band-structure energy and the repulsive potential energy contributions of the total energy are given.
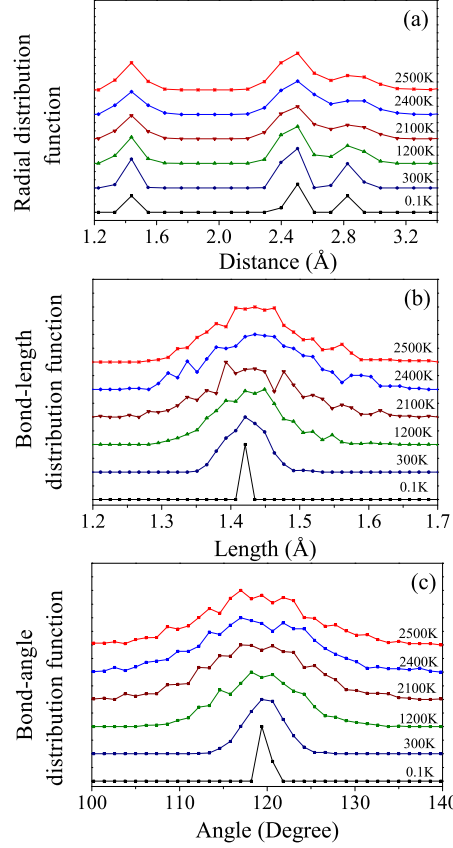
Figure 3. Physical properties obtained in gradual heating: (a) Radial distribution functions, (b) Bond-length distribution functions, c) Bond-angle distribution functions.

temperature. The variation of kinetic energy as a function of temperature yields a fixed value 1.3×10^{-4}eV/K that is in accord with the equipartition theorem (Eq.2). As a result total energy increases as the temperature rises and the variation of energy as a function of temperature yields 3×10^{-4}eV/K. This is in agreement with the only available result in literature for fullerenes [16].

In Figure 3, we show the changes in the physical properties of our SWCNTs change temperature that are displayed through the radial distribution functions, bond-length and bond-angle distribution functions, respectively. . In Figure 3(a) at 300K, we observe the first peak at the nearest neighbor distance of $1.44\mathring{A}$, the second peak is at the second nearest neighbor distance of $2.50\mathring{A}$ and the third peak at $2.82\mathring{A}$. These values are all in accord with the observed properties of $(10, 10)$ tubes [17]. As the temperature is increased a broadening of the first peak is observed. Second peak is deformed and the third peak is almost lost, suggesting that the crystalline phase has been transformed to the amorphous phase. Bond-length distribution function peaks around $1.42\mathring{A}$ which is the a_{c-c} distance for the $(10, 10)$ tube at 300K. The temperature increase affects the peaks that are broadened and do not remain sharp above 1200K. Hexagons of
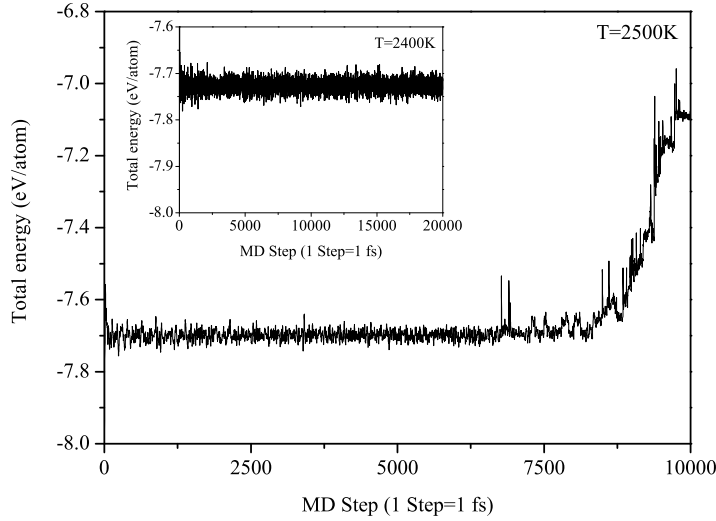
Figure 4. (a) Total energy per atom of the optimized (10,10) SWCNT at 2400K and (b) at 2500K.

carbon atoms are deformed largely until the bond-breaking temperature of 2500K. In Figure 3(b) the peak at 2500K is the bond length distribution obtained before the detachment of atoms begin. Bond-angle distribution function peaks at 119.4 degree at 300K. As the temperature increases peak positions are shifted and peaks are broadened. Above 1200K peaks are no longer sharp. During our simulations we also used a fast heating method that we call "thermal equilibrium method" to check the bond-breaking mechanism of (10,10) SWCNT with temperature increase. In this method, (10,10) SWCNT ought to be optimized at discrete temperature values. We chose the same target temperatures as in gradual (slow) heating. Optimized tubes are left to reach thermal equilibrium at these temperature values. Figure 4 shows that the tube is stable at 2400K. However, the optimized tube left in thermal equilibrium at 2500K is not stable after 7 ps of equilibration time. At the same temperature with gradual heating, after 7 ps of equilibration time atoms start to get detached and as the simulation proceeds the number of detached atoms increase.

We calculated the average radius of the (10,10) SWCNT as $6.785\text{\AA}$ at 300K in accordance with literature. Average radius increases with temperature. (Nanotube length will also change accordingly since we are using NVT algorithms.) In Figure 5 we present the average diameter enlargement with temperature using both heating methods. Radial thermal expansion coefficient of (10,10) SWCNT is calculated from the linear regions in the temperature range between 300-600 K of these patterns. Using Figure 5(a) radial thermal expansion coefficient is calculated as $0.31 \times 10^{-5}(1/K)$. This is the result of gradual (slow) heating method. Using Figure 5(b) we calculated this value as $0.089 \times 10^{-5}(1/K)$. This is the result of thermal equilibrium (fast heating) method. The
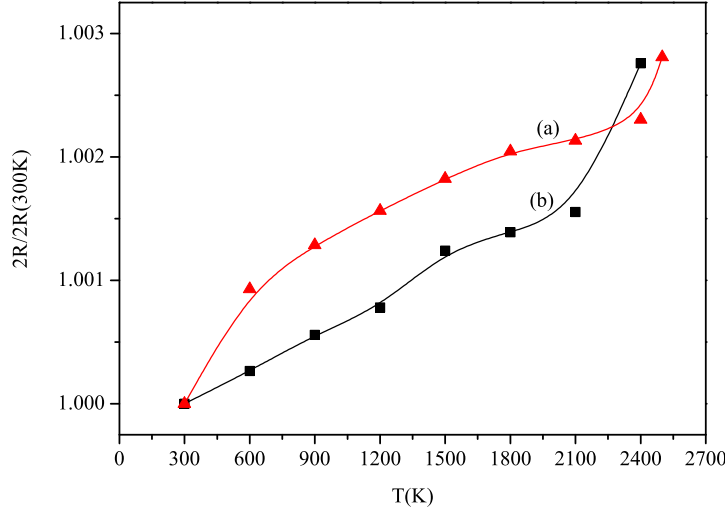
Figure 5. Diameter enlargement with temperature: (a) gradual (slow) heating method, b) thermal equilibrium (fast heating) method.
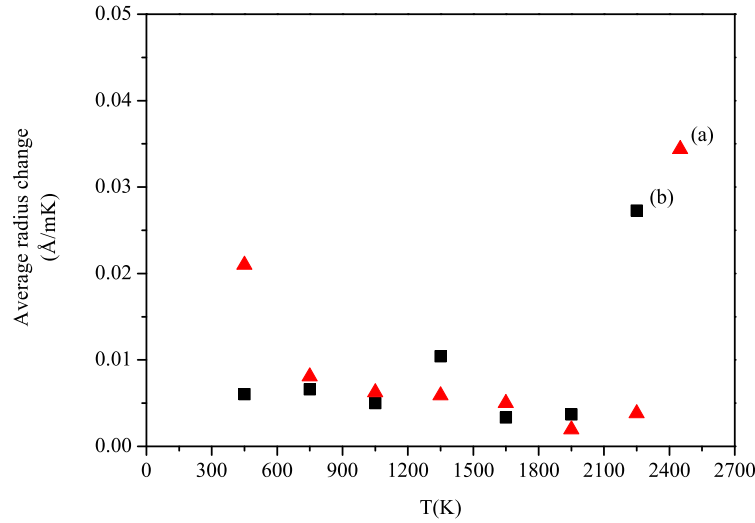
Figure 6. The temperature dependency of average radius change: (a) gradual (slow) heating method, (b) thermal equilibrium (fast heating) method.

temperature-dependency of the thermal expansion indicated in Figure 5 may be shown by taking the derivative of radius-temperature curves. The temperature-dependency of average radius change is illustrated in Figure 6. In the literature, several groups have reported contradicting experimental and MD simulation results for the radial thermal expansion of CNTs [18-21]. Maniwa et al. [18] performed X-ray diffraction (XRD)

studies for the thermal expansion of SWCNT bundles. They determined the radial thermal expansion coefficient as $(-0.15 \pm 0.20) \times 10^{-5}(1/\text{K})$ for SWCNT bundles. On the other hand, the experimental and MD simulation results of Raravikar et al. [19] calculated the radial thermal expansion coefficient as $0.08 \times 10^{-5}(1/\text{K})$. Using a different MD simulation method Schelling et al. [20] also reports the same value. Negative radial thermal expansion coefficient of [21] is commented on by [22-24]. Our radial thermal expansion coefficient value found from the "gradual (slow) heating" method gives a value consistent with [18]. On the other hand "thermal equilibrium (fast heating)" value of $0.089 \times 10^{-5}(1/\text{K})$ is exactly the same as given by [19,20]. This shows the importance of the choice of a heating procedure between 300K and 600K. The temperature-dependency of average radius change as illustrated in Figure 6 shows that after 600K, both methods give the same value of $0.089 \times 10^{-5}(1/\text{K})$.

4. Conclusion

We investigated the thermal characteristics of (10,10) SWCNT using our O(N) TBMD simulation method. First we focused on the effects of temperature change on physical properties such as bond angle, bond length and radial distribution functions; structural stability and the energetics of the tube. We showed that the tube was deformed with increasing temperature but sustained its structural stability up to high temperatures around 2500K. Both the kinetic energy and band structure energy increase while repulsive potential energy decreases as the temperature rises. The variation of kinetic energy as a function of temperature yields a fixed value given by $1.3 \times 10^{-4}\text{eV/K}$ in accordance with the equipartition theorem (Eq.2). As a result total energy increases as the temperature rises and the variation of energy as a function of temperature yields $3 \times 10^{-4}\text{eV/K}$ in agreement with Kim et al.'s [16] results for fullerenes. At low temperatures we observed that the bond angle and bond length between carbon atoms have the values 119.40 degree and $1.42\mathring{A}$, respectively. These are in accordance with the hexagonal lattice of SWCNTs made up of graphene sheets. We also investigated the radial distribution functions of the tube and determined that the first third neighboring atoms locate at distances for a reference atom at $1.44\mathring{A}$, $2.50\mathring{A}$, $2.82\mathring{A}$, respectively. With increasing temperature, because of the thermal motions of atoms in the lattice we observed that the atomic vibrations lead to changes in bond-angle, bond-lengths and radial distribution functions. Also from the temperature dependence of radial distribution functions results, we propose that the variation of the third nearest neighbor position shows the thermal expansion of the tube in radial direction. We further determined the enlargement of the tube diameter with increasing temperature. We observed an increase from 1.357 nm to 1.361 nm within the temperature range from 300K to 2400K, in agreement with the experimental results of Yudasaka et al. [25]. Gradual (slow) heating and the thermal equilibrium (fast heating) methods calculate the radial thermal expansion coefficient in the temperature range between 300K-600K as $0.31 \times 10^{-5}(1/\text{K})$ and $0.089 \times 10^{-5}(1/\text{K})$, respectively. As the temperature increases,

gradual (slow) heating result approaches the thermal equilibrium (fast heating) result of 0.089×10^{-5}(1/K). Our gradual (slow) heating simulations corresponds to thermal processes performed using conventional hot-wall furnaces in which temperatures are applied slowly. On the other hand thermal equilibrium (fast heating) simulations bring SWCNTs to a high temperature rapidly. The general trend in thermal processing is to reduce the process temperature and duration as much as possible in order to restrict the motion of atoms through atomic diffusion. Fast thermal processing restricts the diffusion which is important when the control of impurities in the process is important. Fast thermal processes are important for semiconductor device technology. Experimentally, non steady-state investigation methods has been intensively applied to the study of melting of graphite. Fast heating enables one to obtain equilibrium thermal properties such as enthalpy of melting, melting heat as well as temperature. Additional structural features that affect the measurement of melting temperature especially in the vicinity of melting point requires pulsed heating experiments. Pulsed laser heating of graphite shows an absence of a melting temperature plateau in the heating of low density graphite specimen. Carbon vapor, as a result of graphite sublimation, usually plays a leading role in the temperature measurements near the melting point under gradual heating [26]. Through our fast and slow heating simulations of SWCNTs we draw attention to this issue.

5. Acknowledgement

6. References

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